Chem 7800, LSU

Mini-series on "Polymer Scaling", March 2-30, 2004

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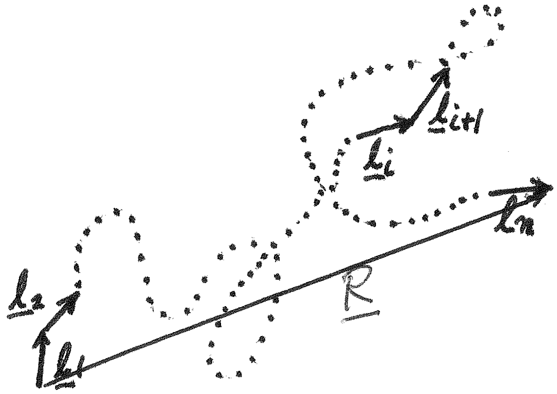
Linear Dimension of Ideal Chain Models

A. Freely-jointed chain:



ETE Vector $\underline{R} = \sum_{i=1}^{n} \underline{l}_i$, $|\underline{l}_i| = |\underline{l}_j| = l$

MS ETE vector

$$\langle R^2 \rangle = \langle (\sum_i^n \underline{l}_i) \cdot (\sum_j^n \underline{l}_j) \rangle$$

$$= \sum_{k=1}^{n} l_k^2 + \sum_{i=1}^{n}\sum_{j=1}^{n} \langle \underline{l}_i \cdot \underline{l}_j \rangle$$

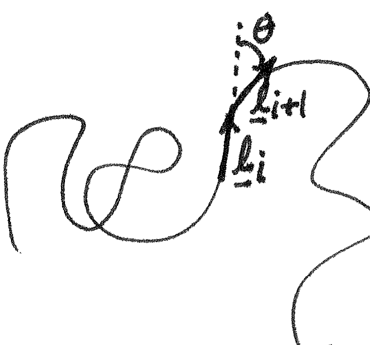
$$= nl^2 + \sum_{i=1}^{n}\sum_{j=1}^{n} l^2 \langle \cos\theta_{ij} \rangle$$

$$= nl^2 + 2\sum_{j=2}^{n}\sum_{i=1}^{j-1} l^2 \langle \cos\theta_{ij} \rangle$$

$$= nl^2$$

For $\langle \cos\theta_{ij} \rangle = \int_0^{\pi} \cos\theta_{ij} \cdot \sin\theta_{ij}\, d\theta_{ij} = 0$

B. Freely-rotating chain:



$0 \le \phi \le 2\pi$, $0 \le \theta \le \pi$

$\underline{l}_{i+1}$ lies anywhere on the surface of the cone with polar angle θ

$$\langle \underline{l}_i \cdot \underline{l}_{i+1} \rangle = l^2 \cos\theta$$

$$\langle \underline{l}_i \cdot \underline{l}_{i+2} \rangle = l^2 \cos^2\theta$$

$$\vdots$$

$$\langle \underline{l}_i \cdot \underline{l}_{i+k} \rangle = l^2 \cos^k\theta$$

$$\vdots$$

$$\langle \underline{l}_1 \cdot \underline{l}_n \rangle = l^2 \cos^{n-1}\theta$$

$$\langle R^2 \rangle = \sum_{k=1}^{n} l_k^2 + 2\sum_{j=2}^{n}\sum_{i=1}^{j-1} \langle \underline{l}_j \cdot \underline{l}_i \rangle$$

$$= nl^2 + 2l^2 \left[\sum_{k=1}^{n-1} (n-k) \cdot \cos^k\theta \right]$$

$$= nl^2 + 2l^2 \left[(n-1)\cos\theta + (n-2)\cos^2\theta + (n-3)\cos^3\theta + \ldots + (1)\cos^{n-1}\theta \right]$$

$$= nl^2 + 2l^2 \left[\sum_k (n\alpha^k - k\alpha^k) \right]$$

Let $\alpha \equiv \cos\theta$

Bond vector dot products matrix

$$\begin{pmatrix} 11 & 12 & 13 & 14 & \cdots & 1n \\ 21 & 22 & 23 & 24 & \cdots & 2n \\ 31 & 32 & 33 & 34 & \cdots & 3n \\ \vdots & & & & & \vdots \\ & & & & & n\text{-}1\,n \\ n1 & n2 & n3 & n4 & \cdots & nn \end{pmatrix}$$

$(1)\alpha^{n-1}$

$\vdots$

$(n-2)\alpha^2$

$(n-1)\alpha$

self products, nl^2

$$\langle R^2\rangle = nl^2 + 2l^2\left[n\sum_{k=1}^{n-1}\alpha^k - \sum_{k=1}^{n-1}k\alpha^k\right], \quad \alpha<1$$

Let $S \equiv \sum_{k=1}^{n-1}\alpha^k = \alpha+\alpha^2+\alpha^3+\cdots+\alpha^{n-1}$

$$(1-\alpha)^{-1} = 1+\alpha+\alpha^2+\alpha^3+\cdots+\alpha^{n-1}+\alpha^n(1+\alpha+\alpha^2+\cdots)$$
$$= 1+S+\alpha^n\left(\frac{1}{1-\alpha}\right)$$
$$S = \frac{1}{1-\alpha} - 1 - \alpha^n\frac{1}{1-\alpha} = \frac{1-1+\alpha-\alpha^n}{1-\alpha} = \frac{\alpha-\alpha^n}{1-\alpha}$$
$$\sum_{k=1}^{n-1}k\alpha^k = \alpha\frac{d}{d\alpha}\left(\sum_{k=1}^{n-1}\alpha^k\right) = \alpha\frac{d}{d\alpha}\left[\frac{\alpha-\alpha^n}{1-\alpha}\right] = \alpha\frac{(1-n\alpha^{n-1})(1-\alpha)-(\alpha-\alpha^n)(-1)}{(1-\alpha)^2}$$
$$= \frac{\alpha(1-\alpha^n)}{(1-\alpha)^2} - \frac{n\alpha^n}{(1-\alpha)}$$

Thus, $$\sum_{k=1}^{n-1}(n-k)\alpha^k = \frac{n\alpha}{1-\alpha} - \frac{\alpha(1-\alpha^n)}{(1-\alpha)^2}$$

$$\therefore \langle R^2\rangle = nl^2+2l^2\left[\frac{n\alpha}{1-\alpha} - \frac{\alpha(1-\alpha^n)}{(1-\alpha)^2}\right]$$
$$= nl^2\left[\frac{1-\alpha}{1-\alpha} + \frac{2\alpha}{1-\alpha} - \frac{2\alpha}{n}\cdot\frac{(1-\alpha^n)}{(1-\alpha)^2}\right] = nl^2\left[\left(\frac{1+\alpha}{1-\alpha}\right) - \frac{2\alpha}{n}\cdot\frac{(1-\alpha^n)}{(1-\alpha)^2}\right]$$

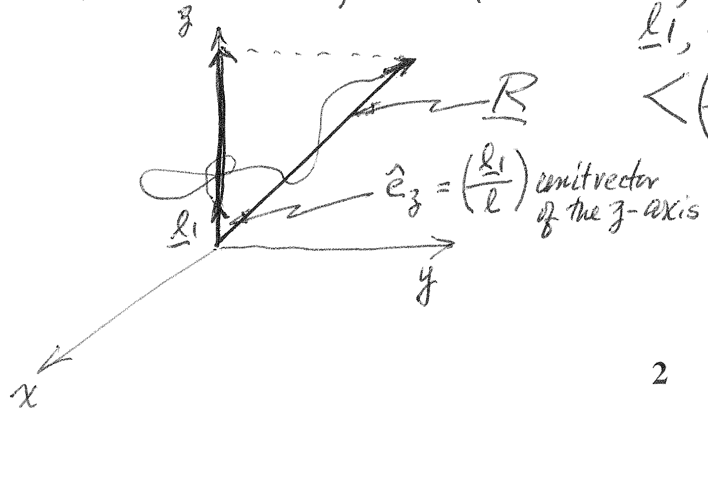
$$\lim_{n\to\infty}\langle R^2\rangle_{frc} = nl^2\left(\frac{1+\alpha}{1-\alpha}\right)$$

For tetrahedral bonding with $\theta = 70°32'$, $\cos\theta = \frac{1}{3}$

$$= nl^2\cdot\frac{4/3}{2/3} = 2nl^2, \quad C_\infty(frc) = 2$$

B. Worm-like coil chain:

Persistence length l_p : Projection of ETE vector $\underline{R}$ along the direction of $\underline{l}_1$, averaged over all configurations of $\underline{R}$



$$\left\langle\left(\frac{\underline{l}_1}{l}\right)\cdot\underline{R}\right\rangle = \frac{1}{l}\left\langle\underline{l}_1\cdot\sum_{i=1}^{n}\underline{l}_i\right\rangle$$
$$= \left(\frac{1}{l}\right)(\underline{l}_1\cdot\underline{l}_1+\underline{l}_1\cdot\underline{l}_2+\cdots+\underline{l}_1\cdot\underline{l}_n)$$

freely rotating chain

$$= \left(\frac{1}{l}\right)l^2(1+\alpha+\alpha^2+\cdots\alpha^{n-1})$$
$$= l\cdot\left(\frac{1-\alpha^n}{1-\alpha}\right)$$

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Thus, the configurational average of ETE vector projection along the first vector direction in the limit of long chain is

$$\lim_{n\to\infty} \langle \hat{e}_z \cdot \underline{R} \rangle = l \cdot \lim_{n\to\infty}\left(\frac{1-\alpha^n}{1-\alpha}\right) = \frac{l}{1-\alpha}$$

which is the definition of persistence length, l_p

Kratky-Porod worm-like chain model:

Chain with arbitrary chain stiffness defined as the limiting continuous case of the freely-rotating chain by letting $l \to 0$ & $\alpha \to 1$ under the constraint that $\left(\frac{l}{1-\alpha}\right)$ remains constant. Thus, $\frac{l}{1-\alpha} \equiv l_p$, $l/l_p = 1-\alpha$, $\alpha = 1 - \frac{l}{l_p} \underset{\substack{l\to 0 \\ l_p \text{ const}}}{\cong} e^{-l/l_p}$

$nl = L = R_{max}$ (contour length of the freely rotating chain)

$\alpha^n \cong e^{-nl/l_p} = e^{-L/l_p}$

1) $\langle R_z \rangle = \langle \underline{R} \cdot \hat{e}_z \rangle = \dfrac{l(1-\alpha^n)}{1-\alpha} = l_p(1 - e^{-L/l_p})$

2) $\langle R^2 \rangle = nl^2\left[\dfrac{1+\alpha}{1-\alpha} - \dfrac{2\alpha}{n}\dfrac{(1-\alpha^n)}{(1-\alpha)^2}\right] \cong 2Ll_p - 2l_p^2(1-e^{-L/l_p})$

$= \dfrac{L}{\lambda} - \dfrac{1}{2\lambda^2}(1-e^{-2\lambda L})$

where $\frac{1}{\lambda} = 2l_p$ (Kuhn segment length)

3) $\langle R^2 \rangle \underset{N\gg 1}{=} Nb^2 \underset{n\gg 1}{=} nl^2\left(\dfrac{1+\alpha}{1-\alpha}\right) \cong nl\left(\dfrac{l}{1-\alpha}\right)2$

$= Ll_p \cdot 2 = 2l_p(Nb)$

$\therefore b = 2l_p$ (Kuhn length $= 2\times$ persistence length)

4) Provided $N \gg 1$

$$P(\underline{R}, N) = \left(\frac{3}{2\pi Nb^2}\right)^{3/2} e^{-3R^2/2Nb^2}$$

Probability density for ETE vector $\underline{R}$ of the renormalized chain